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14. ABSTRACT
Polyhedral Oligomeric Silsesquioxanes are three dimensionally precise silicon/oxygen nanoparticles. These nanoparticles can be tailored to maximize the interactions between the POSS compounds and the polymer by the modification of the organic groups surrounding the inorganic cage. This study examines the ability of POSS to improve the mechanical and surface properties of three semicrystalline polymers, fluorinated ethylene-propylene (FEP), poly(vinylidene fluoride) (PVDF) and isotactic polypropylene (PP). The POSS materials used included $methyl_8T_8$ and two FluoroPOSS compounds, $fluorodecyl_8T_8$ and $fluorooctyl_8T_8$. The FluoroPOSS compounds have been shown to exhibit remarkable surface characteristics, which have been observed in water contact angle measurements. In a comparative study, five and ten weight percent of $methyl_8T_8$ was melt blended into PVDF, FEP and PP and the same weight percent loadings of $fluorodecyl_8T_8$ and $fluorooctyl_8T_8$ were investigated in PVDF and FEP. The addition of $methyl_8T_8$ was found to increase the modulus of FEP and PP, while the incorporation of all three POSS compounds decreased the modulus of PVDF. In addition, the $methyl_8T_8$ in PP increased the tensile strength, Izod impact strength and heat deflection temperature. The injection molded FEP blend samples showed indirect evidence of surface migration, as demonstrated in the core/shell morphology observed in pulled tensile bars and disks for surface analysis. The incorporation of FluoroPOSS into FEP and PVDF drastically increased the hydrophobicity and oleophobicity of those materials.

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DETERMINATION OF MECHANICAL AND SURFACE PROPERTIES OF SEMICRYSTALLINE POLYHEDRAL OLIGOMERIC SILSESQUIOXANE (POSS) NANOCOMPOSITES

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ABSTRACT

Polyhedral Oligomeric Silsesquioxanes are three dimensionally precise silicon/oxygen nanoparticles. These nanoparticles can be tailored to maximize the interactions between the POSS compounds and the polymer by the modification of the organic groups surrounding the inorganic cage. This study examines the ability of POSS to improve the mechanical and surface properties of three semicrystalline polymers, fluorinated ethylene-propylene (FEP), poly(vinylidene fluoride) (PVDF) and isotactic polypropylene (PP). The POSS materials used included $methyl_8T_8$ and two FluoroPOSS compounds, $fluorodecyl_8T_8$ and $fluorooctyl_8T_8$. The FluoroPOSS compounds have been shown to exhibit remarkable surface characteristics, which have been observed in water contact angle measurements. In a comparative study, five and ten weight percent of $methyl_8T_8$ was melt blended into PVDF, FEP and PP and the same weight percent loadings of $fluorodecyl_8T_8$ and $fluorooctyl_8T_8$ were investigated in PVDF and FEP. The addition of $methyl_8T_8$ was found to increase the modulus of FEP and PP, while the incorporation of all three POSS compounds decreased the modulus of PVDF. In addition, the $methyl_8T_8$ in PP increased the tensile strength, Izod impact strength and heat deflection temperature. The injection molded FEP blend samples showed indirect evidence of surface migration, as demonstrated in the core/shell morphology observed in pulled tensile bars and disks for surface analysis. The incorporation of FluoroPOSS into FEP and PVDF drastically increased the hydrophobicity and oleophobicity of those materials.

1. INTRODUCTION

Nanomodification of semicrystalline polymers is a subject of great interest in a variety of industries from the automotive industry to satellite manufacturers. This interest stems from the promise of unequalled thermal, mechanical and surface properties at low volume fractions that cannot be obtained using conventional fillers. The nanoparticles used in this study are polyhedral oligomeric silsesquioxanes (POSS). POSS molecules are three dimensionally precise nanometer sized silicon/oxygen cages with compatibilizing organic groups attached to the inorganic cage. These organic groups are varied to design the most compatible nanoparticles for a particular polymer system (1,2) It has been shown that blending POSS molecules into polymers can increase the thermal and mechanical properties as well as the surface properties of

the polymer blends (3-12). One study of particular interest to the authors was conducted by Bruce Fu and coworkers (3) where they blended methyl$_8$T$_8$ into ethylene-propylene copolymers, in a similar method to the one used by the authors in this study. They found a 70% increase in the Young's Modulus. The investigators postulated that POSS molecules crystallized and these nanocrystals formed weak bonds with the polymer chains. The crystallites are formed due to POSS/POSS interactions, which are well explained by Coughlin and coworkers (13). Further unpublished results indicate that this type of reinforcement is not seen in polyethylene homopolymer blends (14). This suggests that the methyl pendant group on the polymer chain is influencing the reinforcing efficiency of the POSS molecules. The primary reinforcing mechanism in the nanocomposites, POSS/POSS interactions, POSS/polymer interactions or a combination of the two, is a subject for future research. This study examines the effect of blending various POSS molecules into a variety of appropriate semicrystalline polymers. The quality and effectiveness of the blends are characterized by mechanical properties and surface analysis.

2. EXPERIMENTAL

2.1 Materials: The POSS materials used in this study include hydrocarbon and fluorinated compatilizing organic groups (Figure 1). The fluorinated compounds were synthesized at Edwards Air Force Base and include 1H,1H,2H,2H-heptadecafluorodecyl$_8$T$_8$ (Fluorodecyl POSS), 1H,1H,2H,2H-tridecafluorooctyl$_8$T$_8$ (Fluorooctyl POSS). The hydrocarbon modified POSS used in this work is methyl$_8$T$_8$ and was obtained from Hybrid Plastics, Hattiesburg MS. The semicrystalline polymers utilized in this study are both hydrocarbon and fluorinated as well. The fluorinated ethylene/propylene (FEP T-100) was obtained from DuPont, Parkersburg WV and the polyvinylidene fluoride (PVDF Kynar 740) was obtained from ARKEMA Inc., Philadelphia PA. The third polymer investigated is isotactic polypropylene (PP Inspire H704-04) and was obtained from Dow Chemical, Midland MI. (Figure 2)
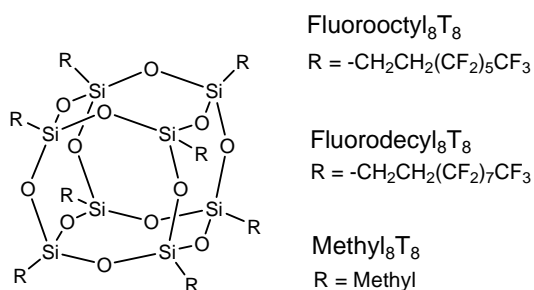

Fluorooctyl$_8$T$_8$
R = -CH$_2$CH$_2$(CF$_2$)$_5$CF$_3$

Fluorodecyl$_8$T$_8$
R = -CH$_2$CH$_2$(CF$_2$)$_7$CF$_3$

Methyl$_8$T$_8$
R = Methyl

Figure 1: POSS cage structure and chemical formulas for organic compatibiliers

2.2. Preparation of Blends: Five and ten weight percent of methyl$_8$T$_8$, Fluorooctyl POSS and fluorodecyl$_8$T$_8$ were melt blended into FEP and PVDF. The same weight percentages of POSS filler were used in making PP/methyl$_8$T$_8$ blends. The fluoropolymer blends were compounded using a DSM Microcompounder and the PP blends were formed using a DSM Minicompounder. Each of these compounders is a conical recirculating twin-screw extruder, with the

microcompounder and minicompounder having capacities of 5 cm^3 and 15 cm^3, respectively. All blends were mixed under nitrogen at a screw speed of 100 RPM. The FEP blends were compounded at 280 ºC for three minutes and the PVDF blends were mixed for three minutes at 180°C. The PP blends were processed for 10 minutes at 220 ºC. The mixed samples were directly molded into various shapes at required for mechanical testing.
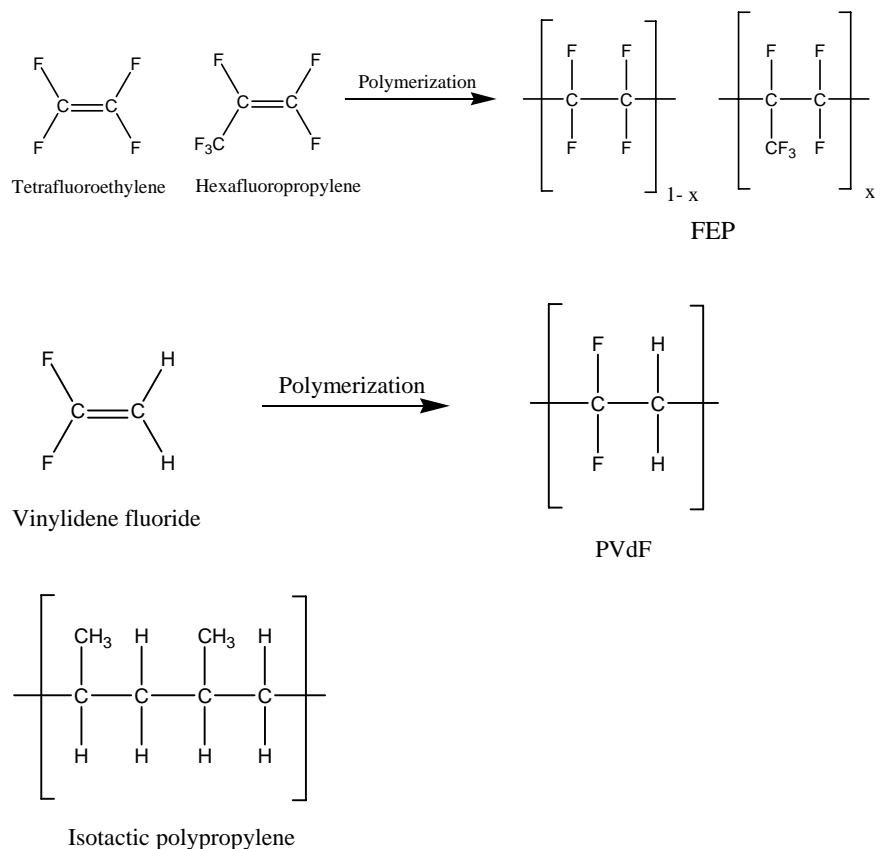
Figure 2: Polymer chemical structures

2.3 Mechanical Properties: The tensile data was gathered for the fluoropolymer samples using a Tinius Olsen H100K-S. Three injection molded tensile bars were used for each sample. Samples were pulled at a crosshead rate of 10 mm/min. The load cell capacity was 10 kN, with a refresh rate of 255 ms. Force and displacement curves were gathered and Youngs modulus was calculated using the initial slope of the curves. The tensile data for the PP samples was obtained using a screw-driven Instron, per ASTM D638 (14). Furthermore, the polypropylene samples were tested for heat deflection temperature, ASTM D648, and Izod impact, ASTM D256A (14). The heat distortion measurements were made using a Rheometrics DMTA V in creep mode and the Izod Impact measurements were made using a Monitor/Impact Tester from Testing Machines Incorporated.

2.4 Surface Analysis: The surface of the fluoropolymer blends was investigated using contact angle measurements. The contact angle measurements were made using an OCA 20 video-based optical contact angle measuring system from Future Digital Scientific, Inc. The contact angles were measured for all of the FEP and PVDF blends. Deionized water was used as the

interrogating liquid to explore the hydrophobicity of the materials. Small drops (4 µl) were dispensed onto injection-molded disks, and captured using the attached camera. Oleophobicity measurements were taken using hexadecane as the interrogating liquid; 2 µl droplets of oil were used.

3. RESULTS AND DISCUSSION

3.1 Mechanical Properties: Tensile properties of the PVDF and FEP blends were investigated using a Tinius Olsen H100K-S. Between three and five tensile bars were pulled for each sample, and the mean and standard deviation were calculated for each blend. Figure 3 shows the mean modulus calculated for the FEP blends. The modulus was calculated based on the initial 0.5 – 1% strain resulting in a straight line (with r sq > 0.99). Error bars are shown for each blend; these represent one standard deviation in either direction.
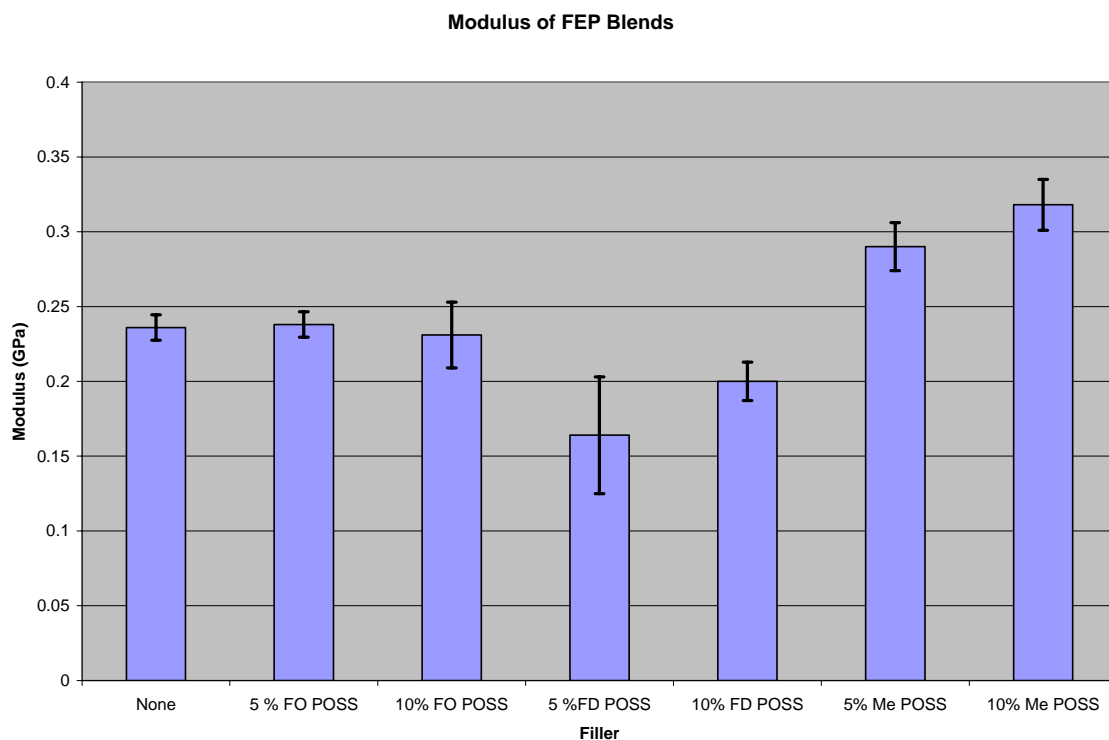
Modulus of FEP Blends

Figure 3: The modulus of the FEP blends is shown. Error bars represent one standard deviation in either direction. FD refers to fluorodecyl$_8$T$_8$, FO refers to fluorooctyl$_8$T$_8$, and Me refers to Methyl$_8$T$_8$.

Methyl$_8$T$_8$ (both five and ten weight percent) blended into FEP yielded a statistically significant increase in the modulus at the 95% confidence level (not shown on graph). Ten weight percent of filler returned a slightly higher mean modulus, but at the 95% confidence level, no significant difference in modulus is observed between five and ten weight percent of filler.

The addition of either five or ten weight percent of fluorodecyl$_8$T$_8$ or fluorooctyl$_8$T$_8$ did not statistically significantly alter the modulus from unfilled FEP. The data gathered for the FEP

filled with either fluorodecyl$_8$T$_8$ or fluorooctyl$_8$T$_8$ was inconsistent, which is reflected in the large error bars. Samples "pulled out" frequently (see Figure 4) and after the surface material flaked away, the interior of the tensile bars frequently elongated to over 150% strain before breaking. In addition, the outer layers of tensile bar often flaked away as soon as any tension was applied to the material. This is indirect evidence of surface migration of the nanoparticles with a core/shell morphology and possible poor nanoparticles dispersion. In the core/shell morphology, each region has vastly different physical properties, which may be due to the different concentrations of nanoparticles.

Nanocomposite blends with FEP and either fluorodecyl$_8$T$_8$ or fluorooctyl$_8$T$_8$ consistently exhibited lower yield points, between 7-8 MPa, when compared to unfilled FEP, 10.5-12.5 MPa range. This is in contrast to the nanocomposite FEP blends with methyl$_8$T$_8$. The yield strengths of the methyl$_8$T$_8$/FEP blends did not show a significant change when compared to the unfilled FEP. In addition, the methyl$_8$T$_8$/PP blends showed an increase in the tensile strength of the material (Figure 5). The contrasting results are due to the different compatibilities of the methyl$_8$T$_8$ with FEP and PP. The methyl$_8$T$_8$ has a higher affinity for the PP and thus has a stronger reinforcing capability similar to the result seen by Fu et al.(3)for ethylene-propylene copolymer.

All fillers added to PVDF significantly lowered the modulus (See Figure 6). Although the PVDF samples did not pull out when tension was applied, but rather elongated until failure. This may imply that there is a uniform concentration of the POSS throughout the sample. This will be investigated in the future. Another observation is that no significant difference was found among the various types of fillers or different loadings.

When the tensile strength of the PVDF blends was examined, it was observed that the unfilled PVDF samples had a slightly higher yield point (40.0 MPa) than did any of the POSS filled samples (36.0-37.5 MPa range).

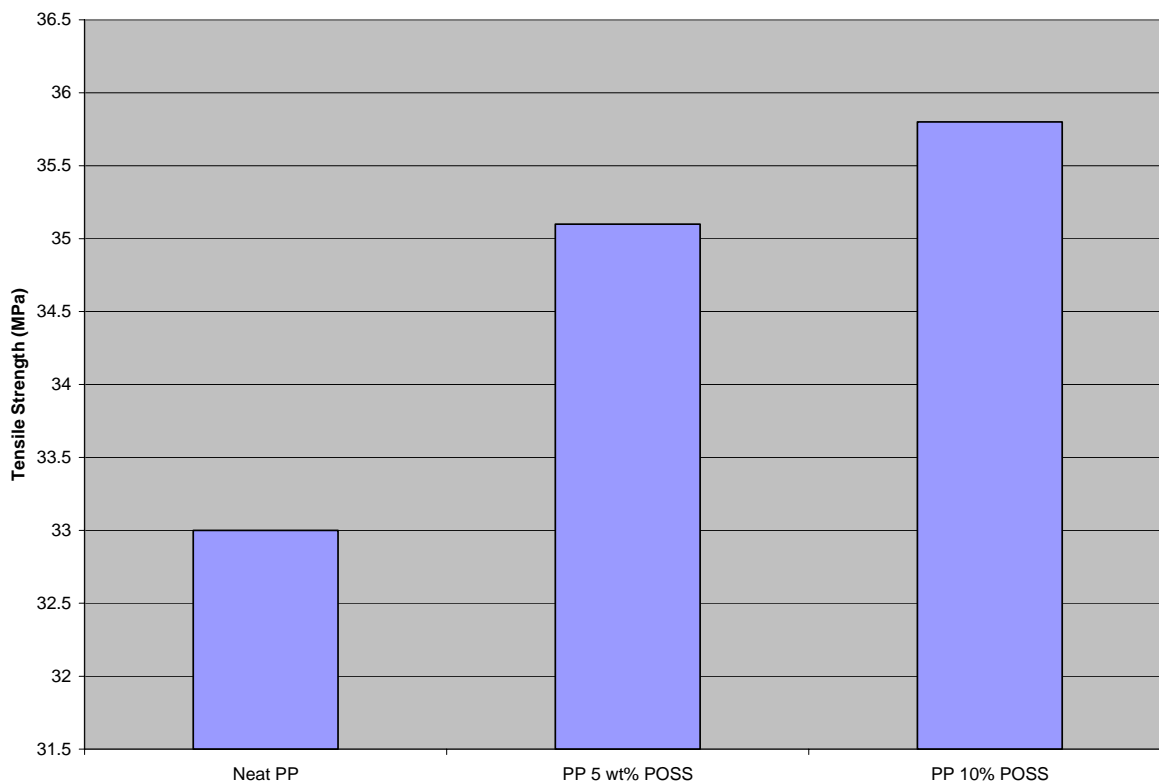**Figure 4:** The failure pattern of above was seen in all FEP blend samples.

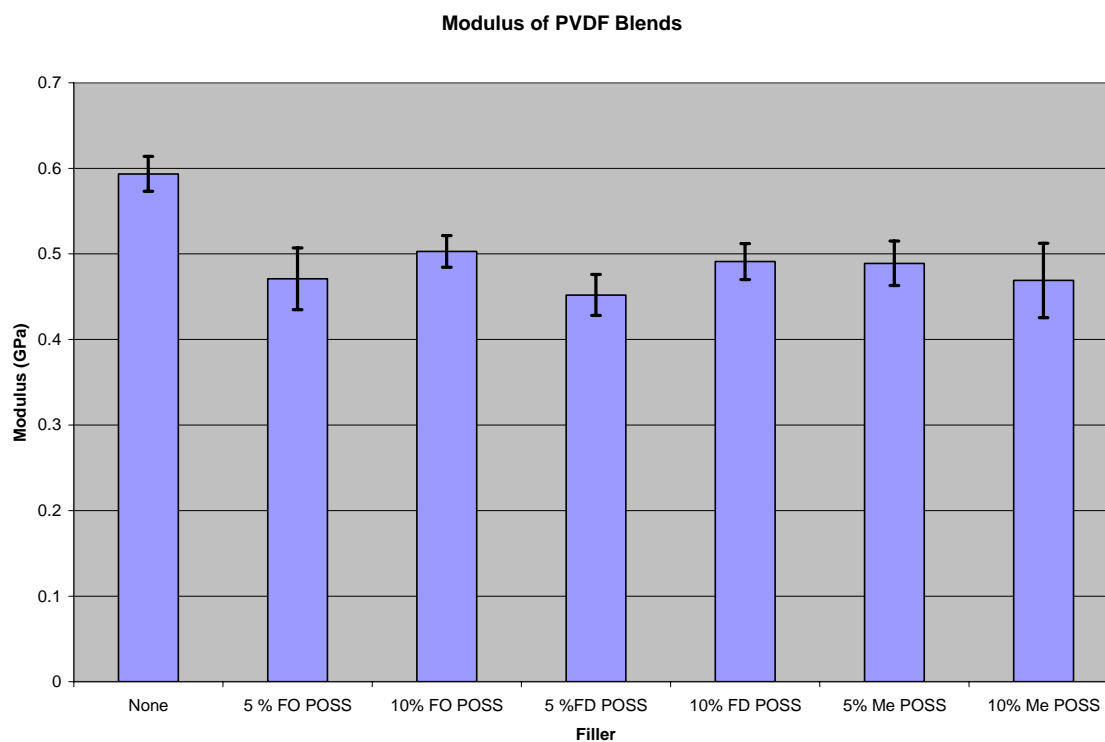**Figure 5:** The tensile strength of the PP blends.

Modulus of PVDF Blends

Figure 6. The modulus of the PVDF blends is shown. Error bars represent one standard deviation in either direction.

In addition to gathering tensile data, the $methyl_8T_8/PP$ blends were subjected to heat distortion testing and impact testing. Heat distortion testing is used to define a use temperature for the material. The addition of POSS to PP yielded a substantial increase, over 20°C, in heat distortion temperature (Figure 7). This increase is due to the interactions between the POSS crystallites and the polymer crystallites. In Figure 8, the authors illustrate that the addition of modulus increasing nanoparticles actually increases the impact properties. This increase in impact strength may be derived from the nanodispersion of the POSS crystallites, which are not large enough to create stress concentrations, and the reinforcing ability of the POSS crystallites.
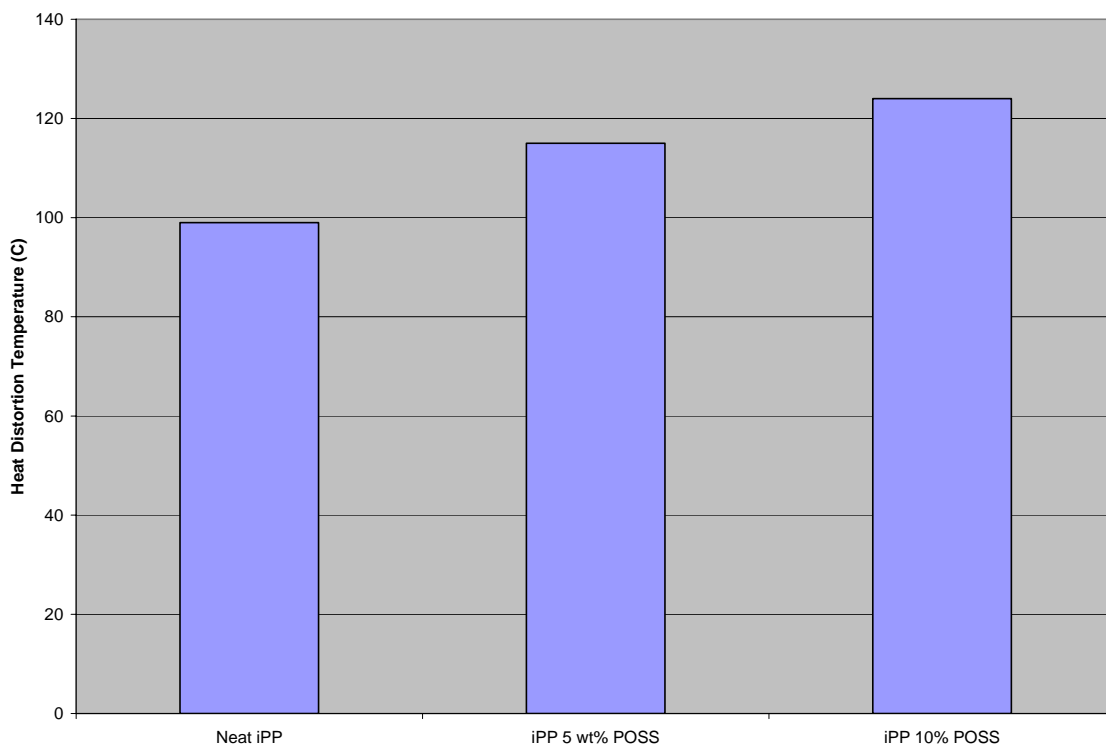

Figure 7: Heat Distortion Temperature results per ASTM D648 @ 4.5 MPa. iPP refers to isotactic polypropylene.
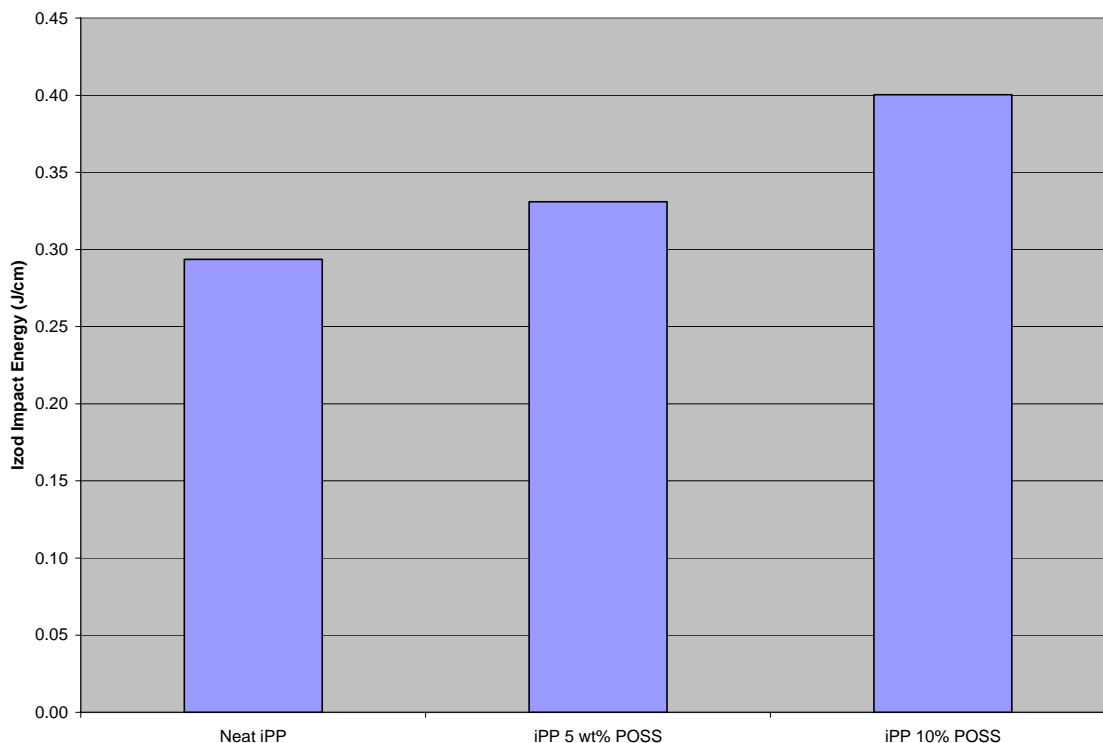
Figure 8: Izod Impact results per ASTM D256A @ 25 ºC

3.2 Surface Properties: The surface properties of PVDF and FEP blends were investigated using water and organic contact angle measurements. Droplet images were captured on the surface of injection molded disks. The surface of the injection molded PVDF blends was smooth and uniform, although flow patterns were visible, especially in the more opaque methyl$_8$T$_8$ blends. All contact angle data can be found in Table 1.

Table 1: Mean water and organic contact angles are shown for the PVDF blends.

PVDF Sample	Average Water Contact Angle (°)	Average Organic Contact Angle (°)
PVDF	73.2	24.7
5 % FO POSS	106	61.7
10% FO POSS	110.6	54.9
5 %FD POSS	106.5	74.3
10% FD POSS	110.8	79.6
5% Me POSS	92.7	23.4
10% Me POSS	94.6	11.3

The unfilled PVDF samples yielded water contact angles between 70-75° (See Figure 9). The addition of fluorodecyl$_8$T$_8$ and fluorooctyl$_8$T$_8$ greatly increased the hydrophobicity of the composites. When five weight percent of either FluoroPOSS material was added the contact angles increased to between 105-110° with the average being reported in Table 1. The addition

of ten weight percent of the nanoparticles yielded angles as high as 116.3° (see Figure 9). While the ten weight percent FluoroPOSS loadings had higher means, at the 95% confidence level, no statistically significant difference was found for between the five and ten weight percent loadings for each nanoparticle. The addition of methyl$_8$T$_8$ to PVDF showed a more modest increase in hydrophobicity, but still an improvement over the unfilled material. No statistically significant difference in the water contact angle was found at the 95% confidence level between the five and ten weight percent blends. This indicates that a volume fraction of POSS additive can greatly affect the surface properties of a PVDF composite material.

The addition, both fluorodecyl$_8$T$_8$ and fluorooctyl$_8$T$_8$ greatly increased the oleophobicity of the PVDF blends. The unfilled PVDF samples yielded contact angles of around 25° (see Figure 10). The addition of fluorodecyl$_8$T$_8$ nanoparticles yielded composites with the greatest increase in contact angle, greater than 50° (Table 1). Furthermore, the addition of methyl$_8$T$_8$ appears to decrease the oleophobicity of PVDF; at the ten weight percent loading, resulting in an oil droplet that nearly spreads completely.

Figure 9: An image of a water droplet on unfilled PVDF (left) is shown next to an image of a water droplet on PVDF blended with ten weight percent fluorooctyl$_8$T$_8$.
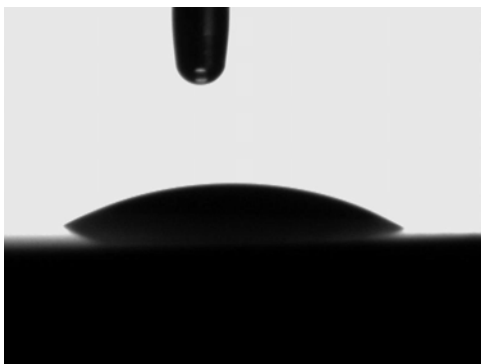

Figure 10: An oil drop is seen on the surface of PVdF.

The FEP samples filled with methyl$_8$T$_8$ yielded contact angles as high as 126.2°. In Figure 11, one will note contact angles of 126.2° and 122.2° for the left and right contact angles respectively. The average water contact angle for the five weight percent methyl$_8$T$_8$ blends was 115° and the average value for the ten weight percent methyl$_8$T$_8$ blends was 120°. This represents an average increase of 19% and 24% over previously compression-molded samples of unfilled FEP[12]. The surface of the injection molded FEP samples, both filled and unfilled, was uneven, with layers of material readily peeling or completely flaking off the disk. Therefore, the results for contact angle measurements were inconsistent for those composite blends. Because the surface was so uneven, samples were polished with very fine sandpaper. On several samples, the top layer of material easily flaked off, revealing the translucent disk. After polishing this surface with very fine sandpaper, the contact angles measured were all in the same range as those found for unfilled FEP samples. This implies that either flow patterns during injection molding or surface migration is pushing the fillers toward the surface.

Figure 11: A water droplet is seen on the surface of and FEP-10% methyl$_8$T$_8$ blend.

4. CONCLUSIONS

A number of Polyhedral Oligomeric Silsesquioxanes (POSS) were melt blended into a variety of semi-crystalline polymers, including fluorinated ethylenepropylene (FEP), isotactic polypropylene (PP), and poly(vinylidene fluoride) (PVDF). These POSS nanomaterials include methyl$_8$T$_8$ and two FluoroPOSS compounds (fluorodecyl$_8$T$_8$ and fluorooctyl$_8$T$_8$).

- The incorporation of both FluoroPOSS compounds into PVDF significantly lowered the modulus, but no significant difference was observed among the different fillers. Slightly lower yield points were observed for the filled versus unfilled PVDF blends.
- The FEP blends showed indirect evidence of surface migration, as evident in core/shell morphology of injection molded tensile bars. The behavior of the tensile bars suggests that the nanoparticles may not be evenly distributed. The only nanofiller that significantly increased the modulus of the FEP blends was methyl$_8$T$_8$, with the ten weight percent loading showing an even greater increase that the five weight percent loading.
- The examination of polypropylene/methyl$_8$T$_8$ revealed that the tensile strength increased with the addition of POSS, heat distortion temperature increased by about 25% and the impact energy increased greater than 35% with the addition of ten weight percent POSS.

- The incorporation of POSS into the fluoropolymers increased both the water and organic contact angles of the polymers, with the exception of the incorporation of methyl$_8$T$_8$ into PVDF, which decreased the oleophobicity of the material.

5. ACKNOWLEDGEMENTS

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